Lead and Copper Corrosion: What have we Learned Since the LCR

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Organization

Recent research advances
  – Lead (brief)
  – Copper
Regulatory balancing act
Future research needs

Lead

“New” Lead (and Copper)Research

USEPA Studies Since 1991

- Effect of ion exchange home water softeners on lead and copper corrosion
- Use of aeration for corrosion control
- Effect of brass alloy composition on the release of metals from the brass (pH, orthophosphate)
- Corrosion control for small systems (silicates, pH adjustment, aeration)
- PbO_2 – lead IV
- Scale analysis database

Aeration for Corrosion Control

- Strip CO_2 from water
- Increase in pH, decrease in DIC
- Decrease in metal solubility
- Simple systems
- Reliable, require little attention
- No addition of chemicals

Aeration for Corrosion Control

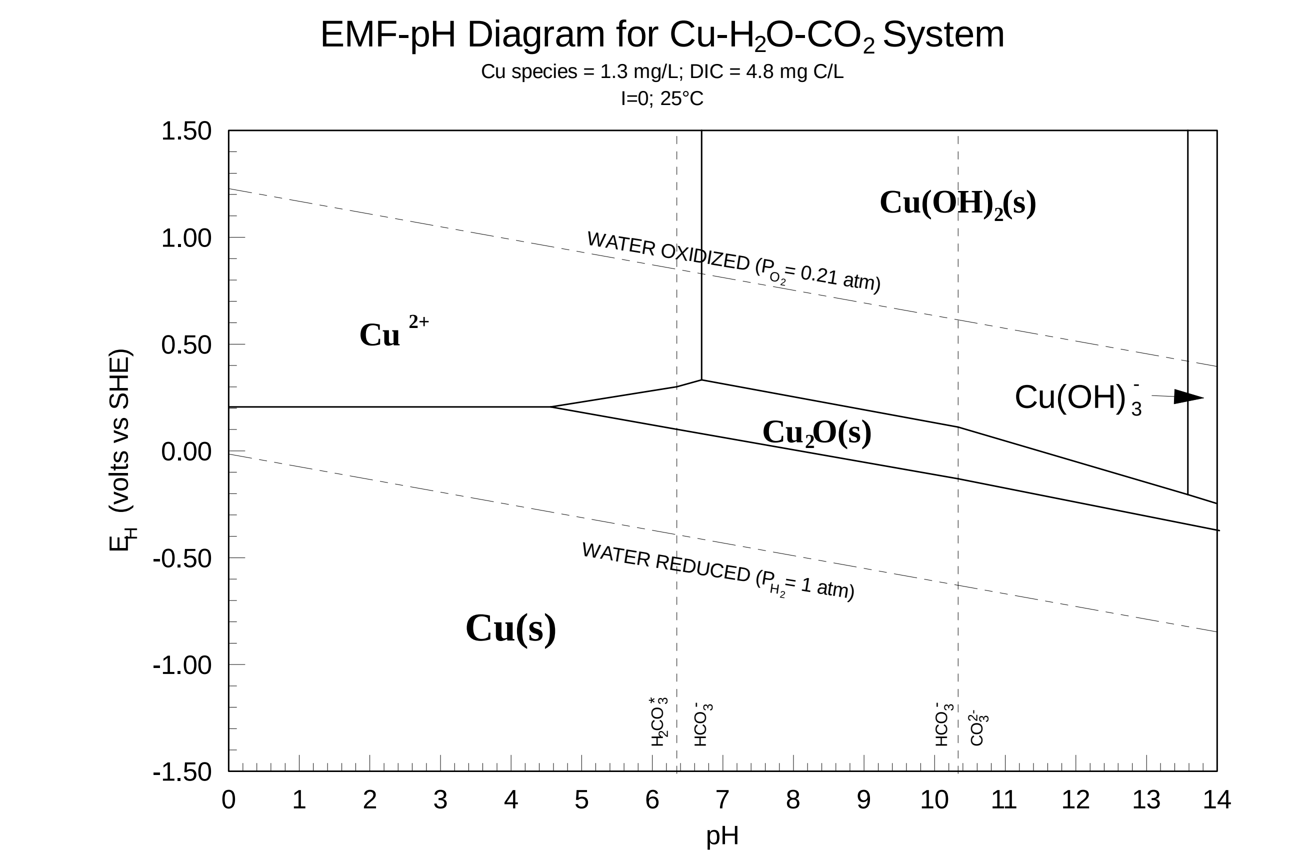
Decision Tree

- pH < 7.2 and DIC > 10 mg C/L? **Maybe**
- Calcium hardness saturation state at goal pH? **Additional treatment**
- Mn > 0.05 mg/L, Fe < 0.2 mg/L? **Additional treatment**
- Radon > 3000 pCi/L? **Additional benefit**

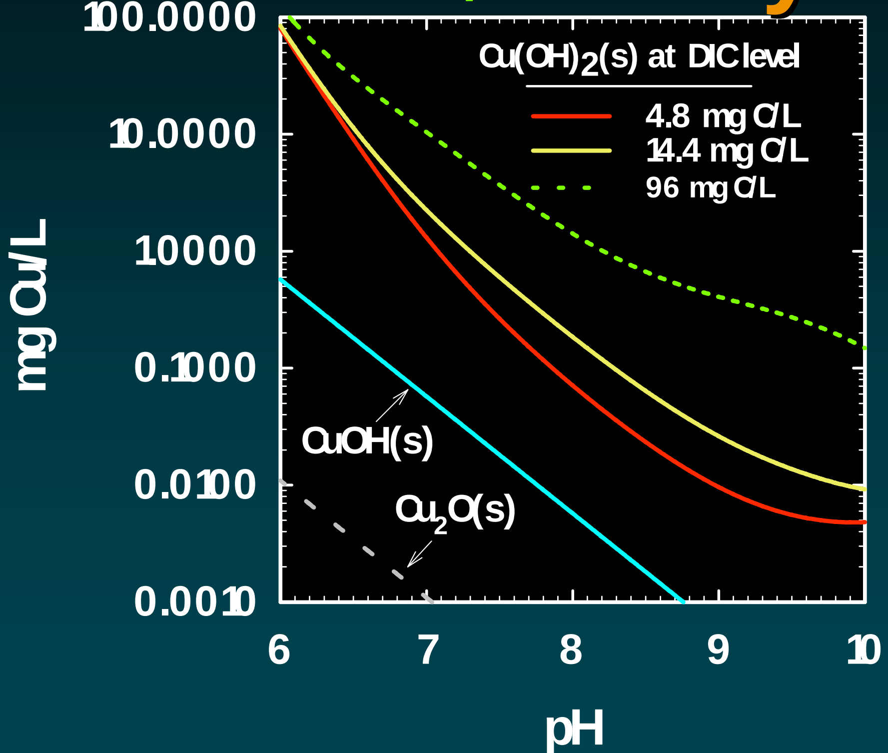
Copper

Copper

Effect of Oxidation-Reduction Potential


EMF-pH Diagram for Cu-H_2O-CO_2 System
Cu species = 1.3 mg/L; DIC = 4.8 mg C/L
I=0; 25°C
E_H (volts vs SHE)
pH
WATER OXIDIZED (P_{O_2}= 0.21 atm)
WATER REDUCED (P_{H_2}= 1 atm)
Cu^{2+}
$Cu(OH)_2(s)$
$Cu(OH)_3^-$
$Cu_2O(s)$
Cu(s)
$H_2CO_3^*$
HCO_3^-
HCO_3^-
CO_3^{2-}

Copper(II) Solubility at Different DIC Levels Compared to Copper(I) Solubility

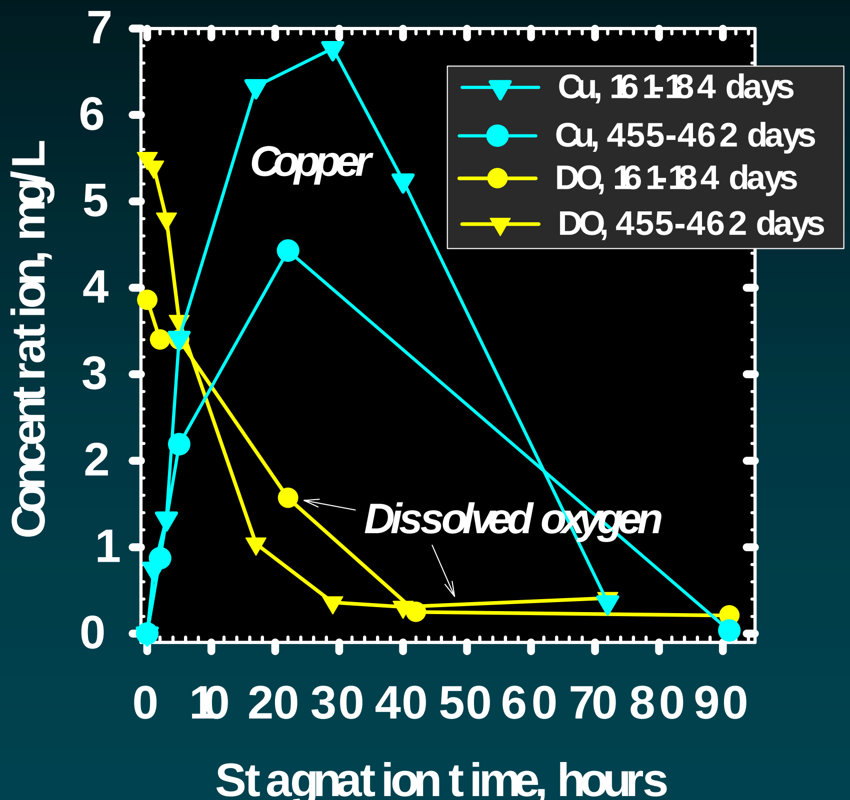


Copper

Effect of Stagnation Time

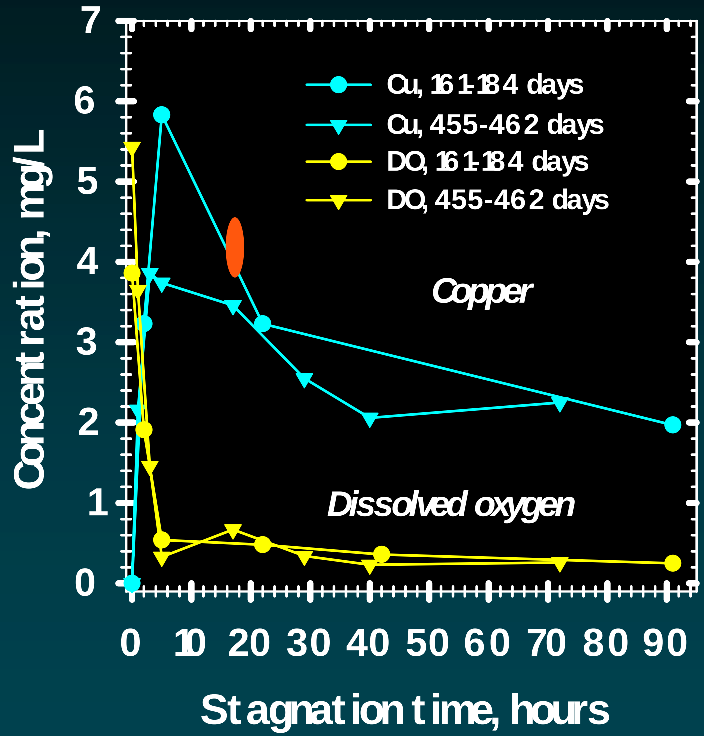
Indian Hill, Ohio, Groundwater

Copper Tubing--Softened Water, DIC=75 mg C/L

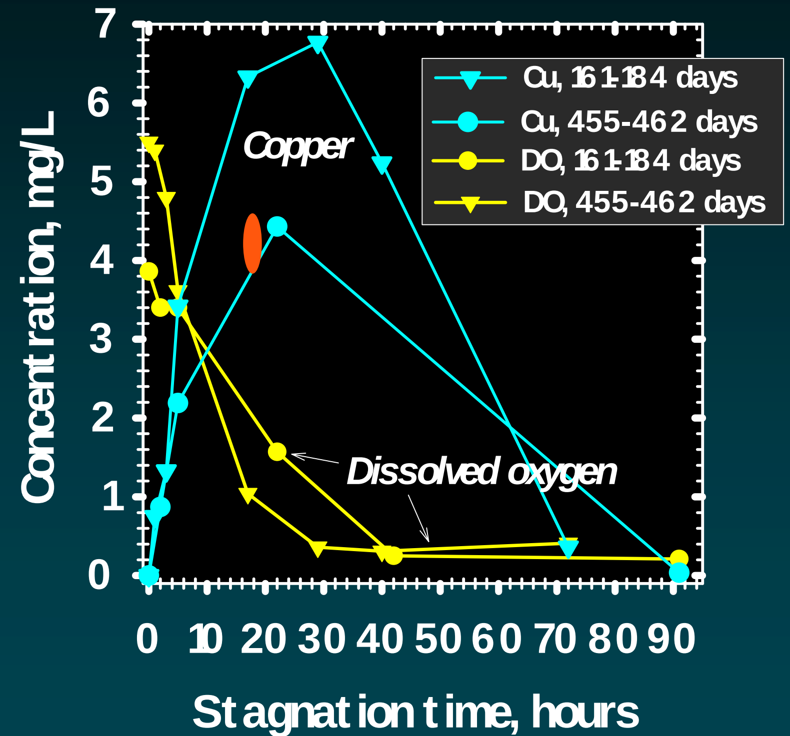


Bias from Sampling Scheme?

Unsoftened water, copper going DOWN

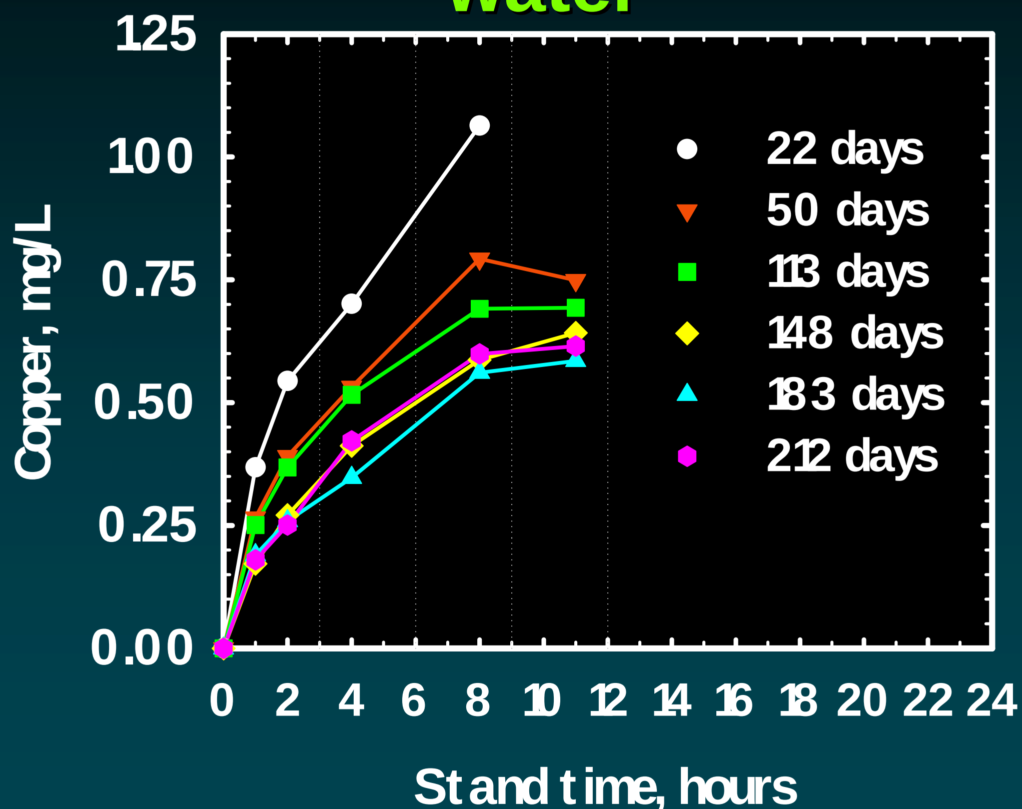


Softened water, copper going UP

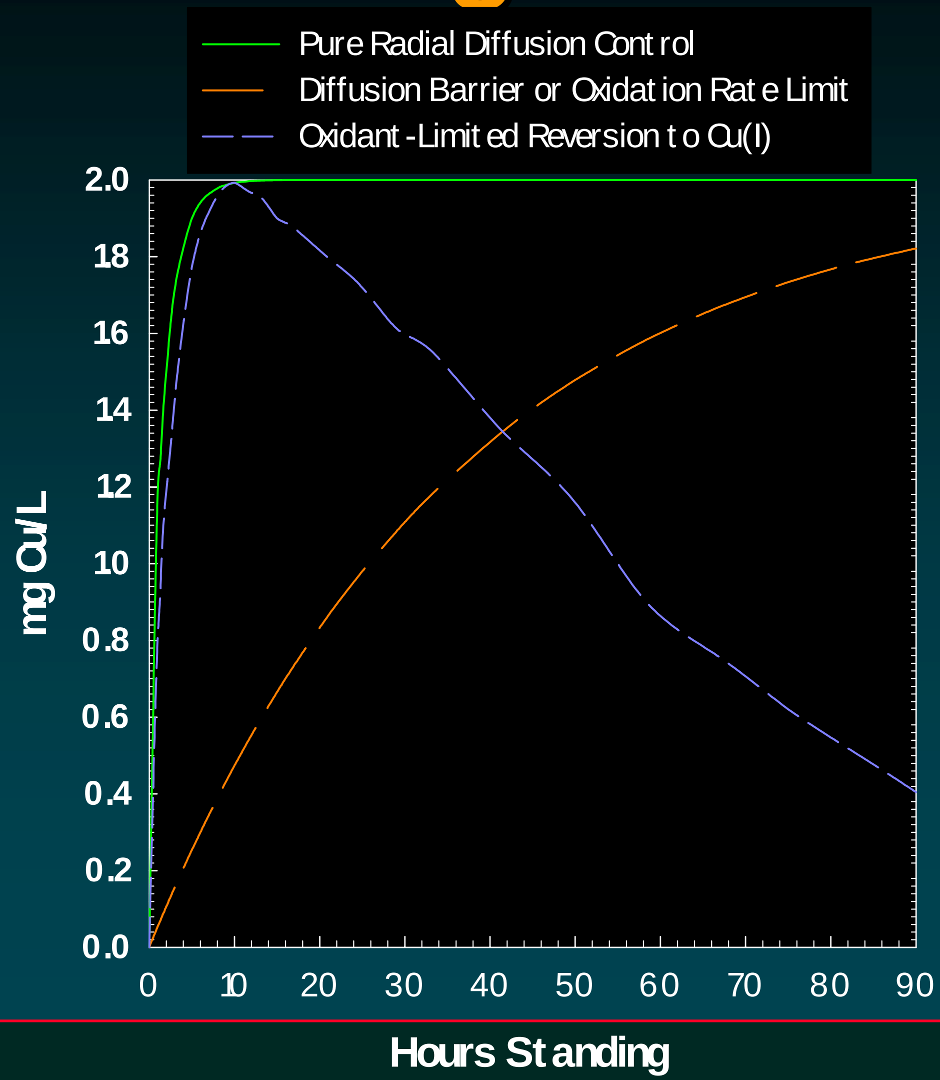


One Age Effect on Stagnation Profile

25 mg/L SiO_2, pH 7.5, Cl_2 + DO, Copper pipe, Tap water



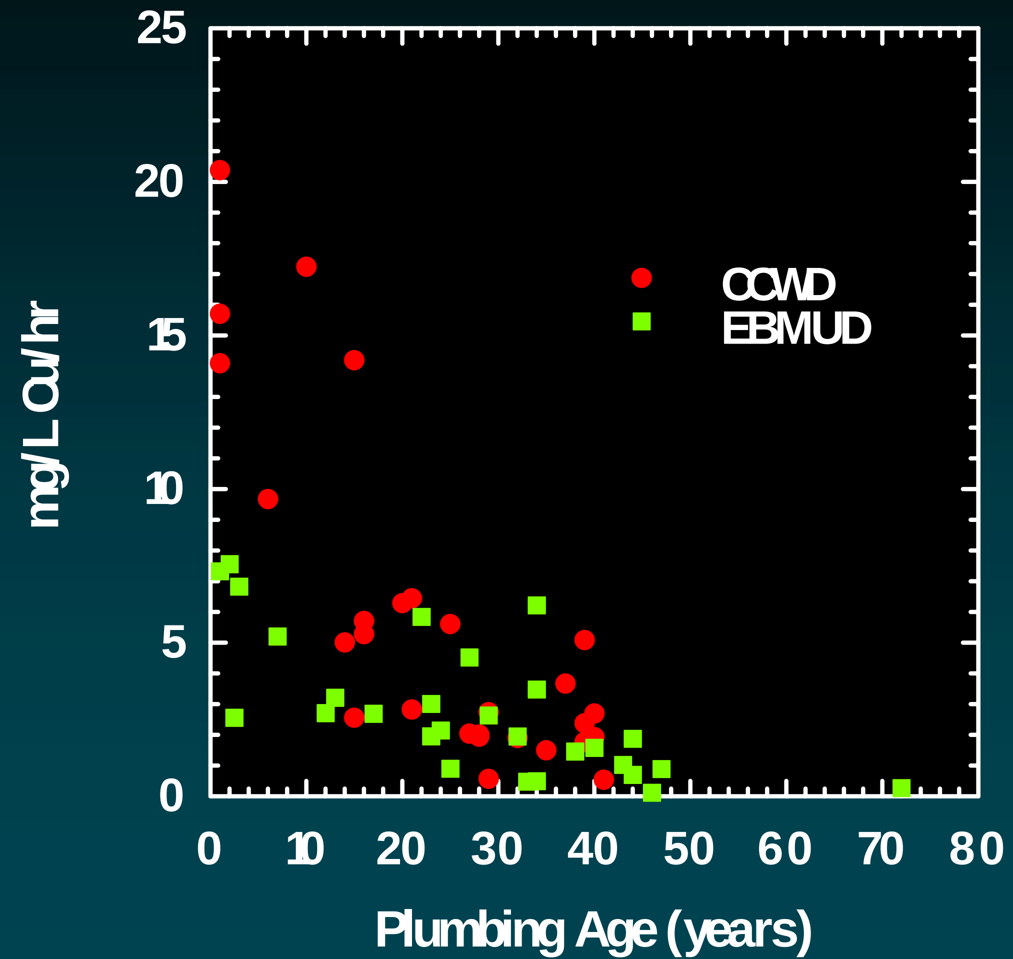
Conceptual Stagnation Profiles



Copper

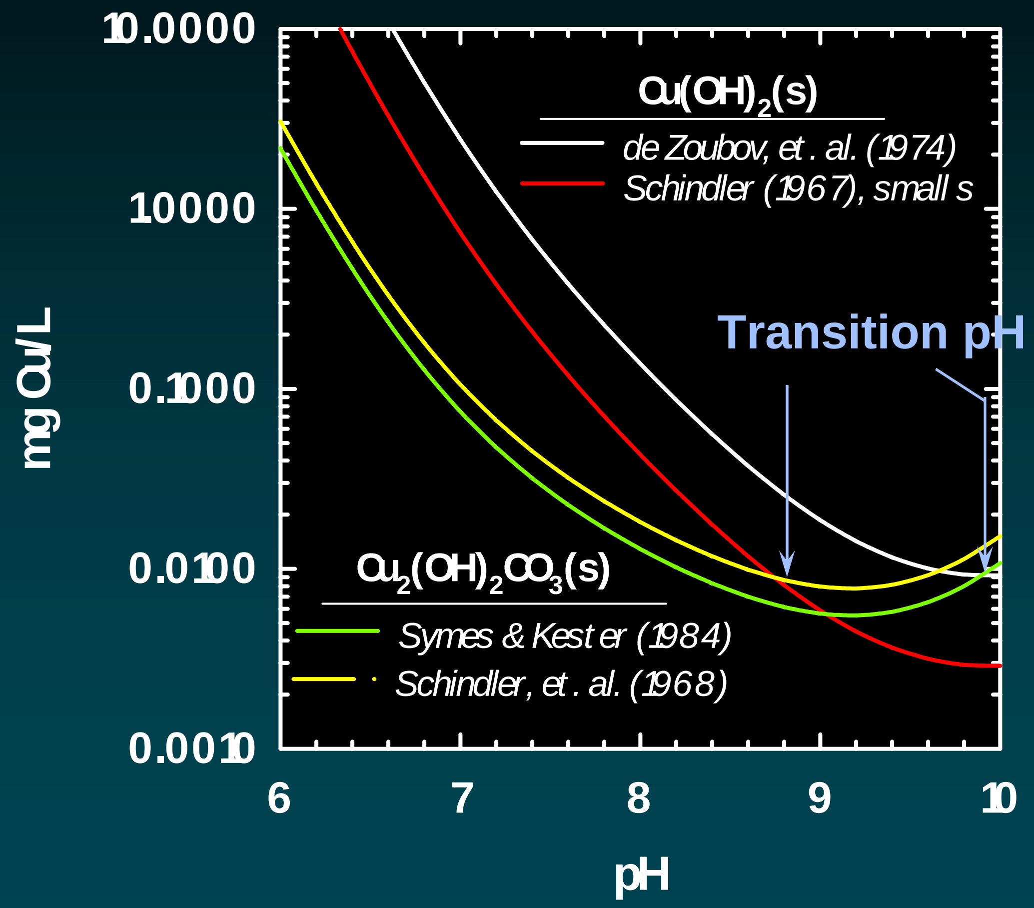
General Chemistry and Aging

Copper Leaching Rate versus Age for California Study

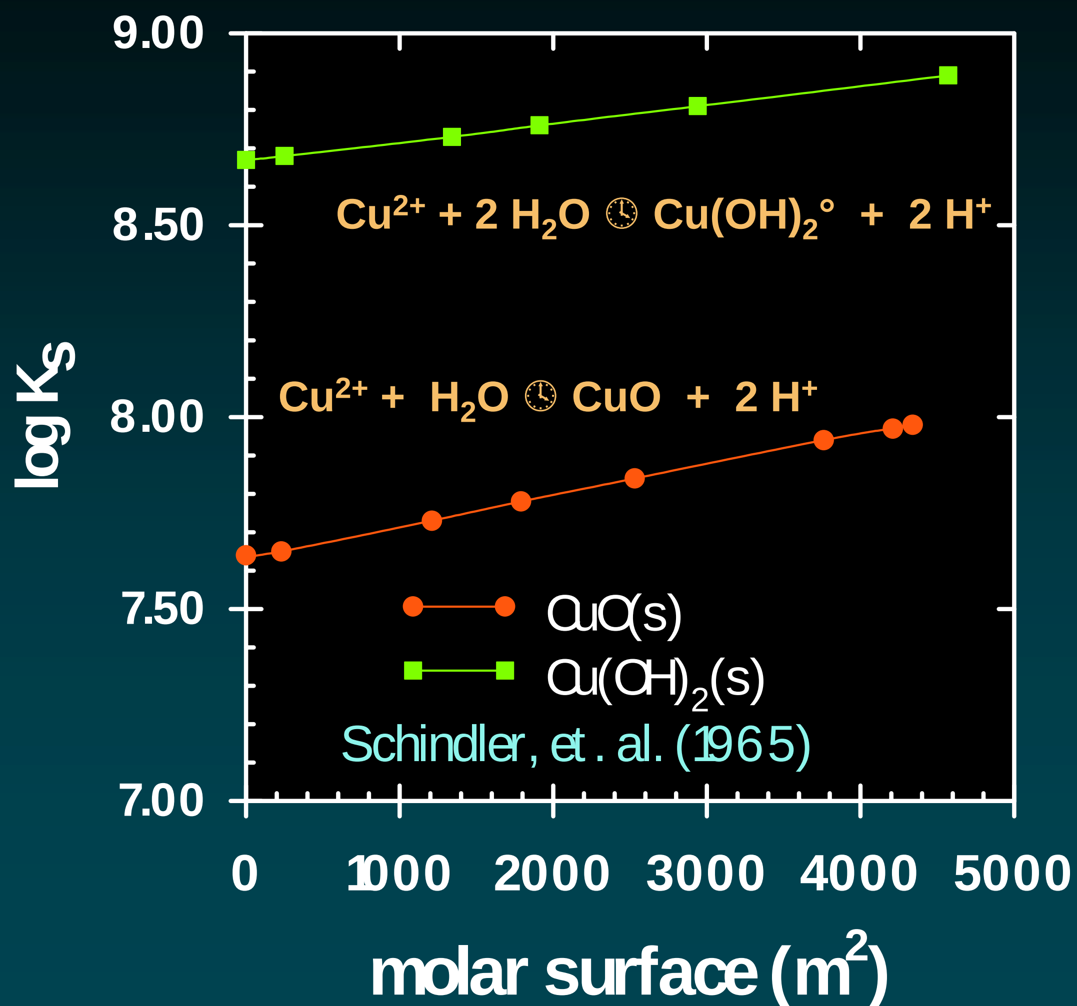


Predicted Copper(II) Solubility by Different Sets of Solubility Constants

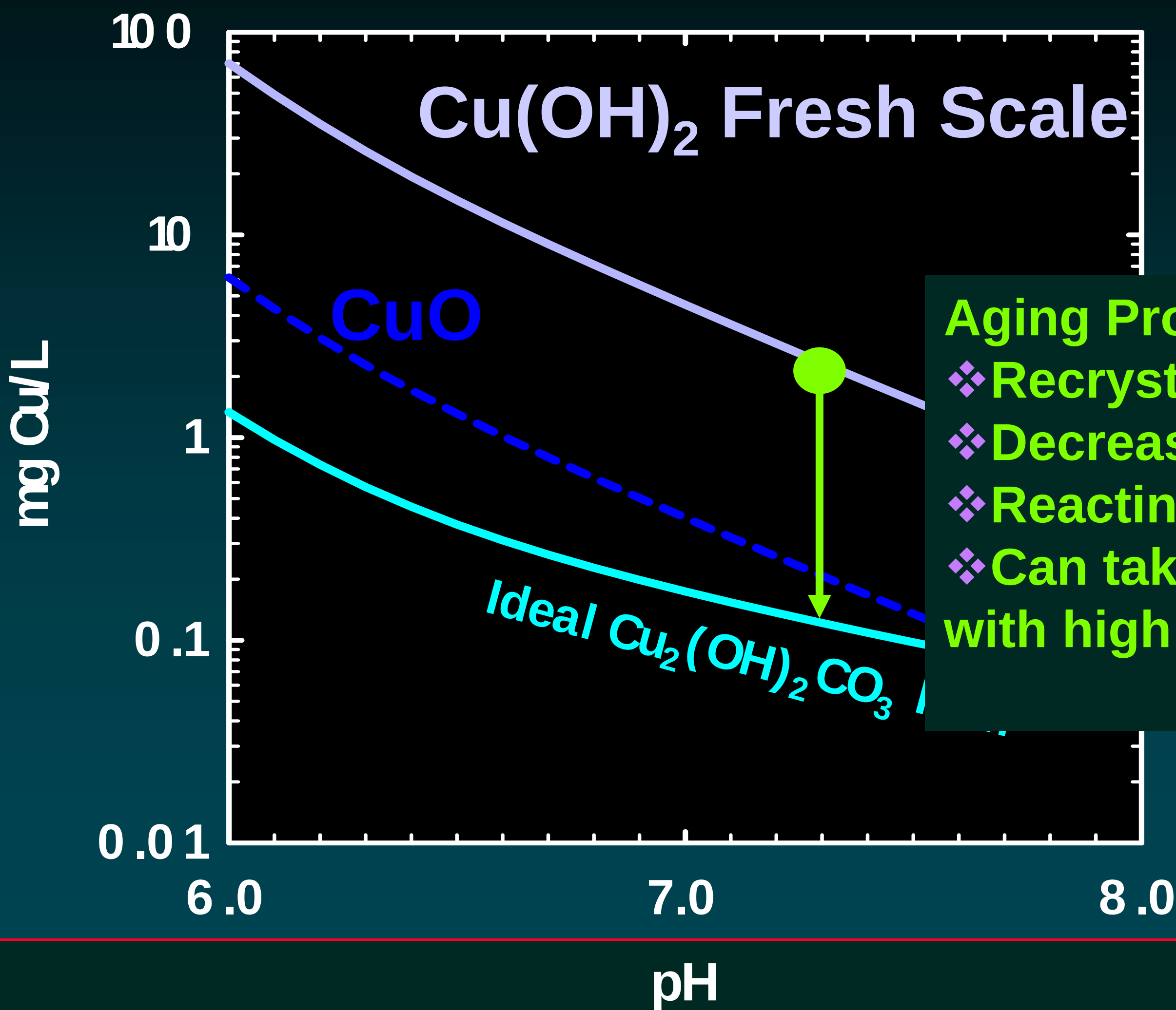
DIC = 4.8 mg C/L, I = 0.005, 25°C



Effect of Molar Surface on Solubility



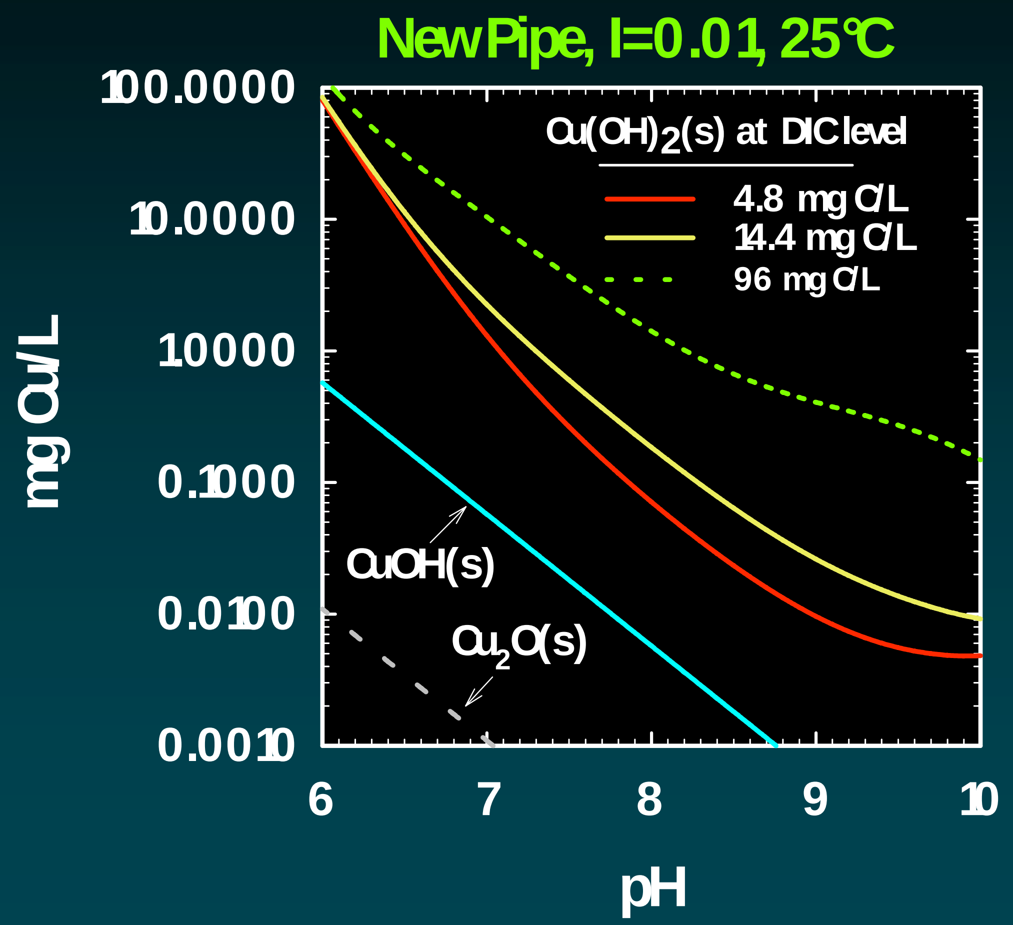
Evolution of Scale Model for High DIC, Low pH



Aging Process (in theory):

- Recrystallizing
- Decreasing surface area
- Reacting with CO_3 or HCO_3^-
- Can take 20, 30 or more years with high DIC

Copper(II) Solubility at Different DIC Levels Compared to Copper(I) Solubility



USEPA Studies

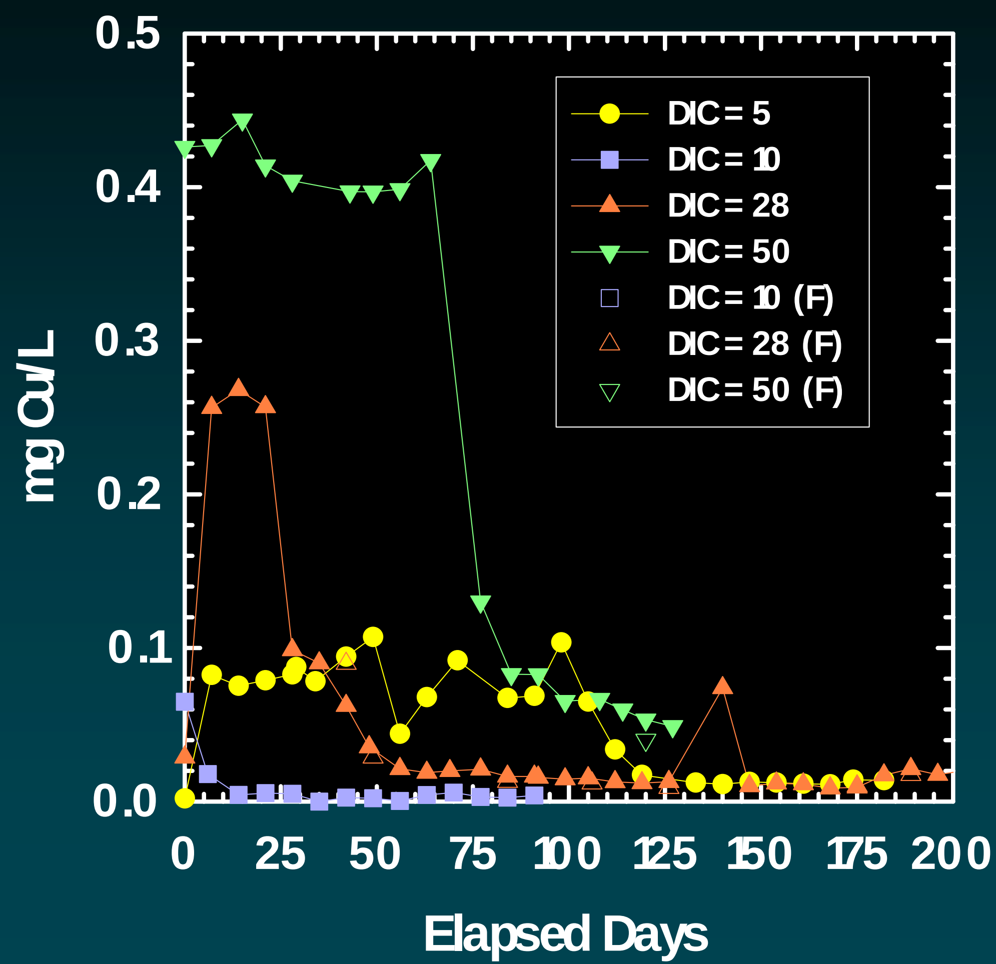
- # Solubility/scale formation phenomena with copper pipe
- # Effect of DIC, pH, Orthophosphate
  – Speciation
  – Solubility
  – Chlorine consumption
  – Mineralogy of corrosion deposits

USEPA Lab Experiments

- pH 6.5, 7.0, 8.0, 9.0
- DIC's 5, 10, 25, 50 mg C/L
- Orthophosphate 0 or 3.0 mg PO_4/L
- Dissolved Oxygen= approx.. 6-7.5 mg/L
- Chlorine residual maintained up to 1 mg/L
- 5 mg/L Calcium in most expts..

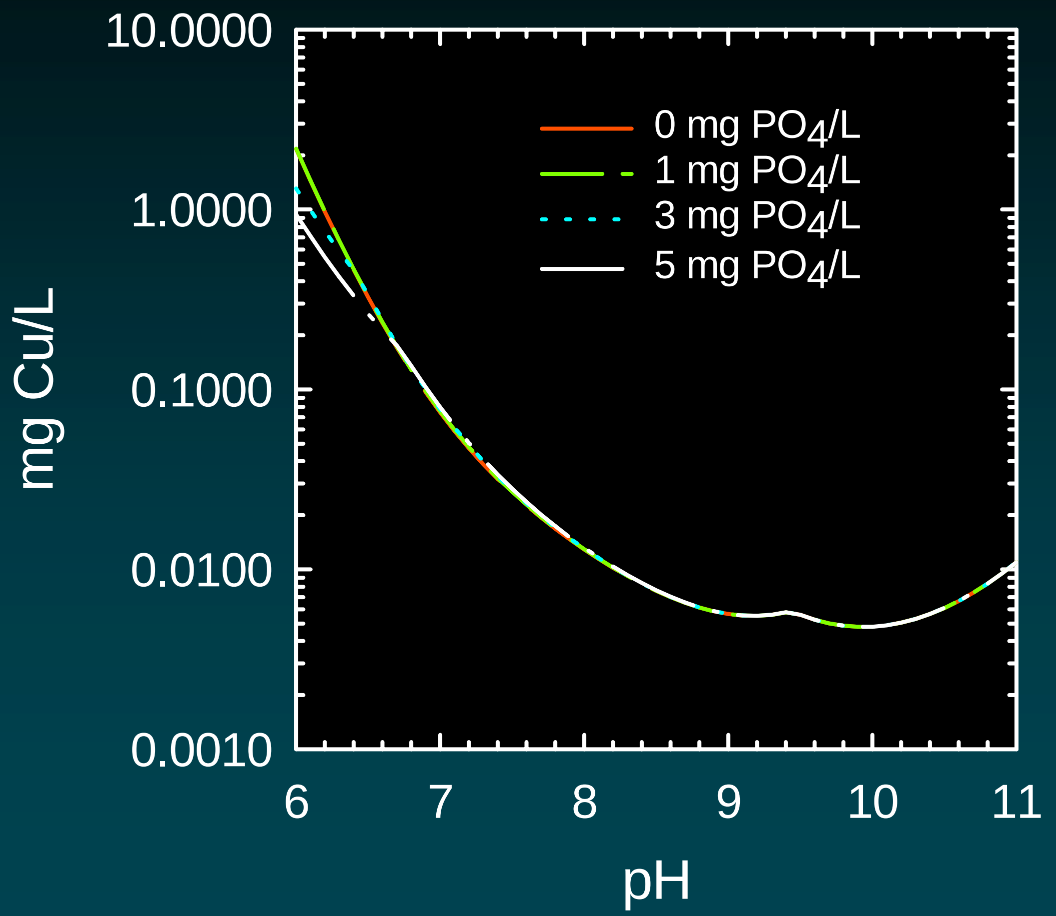
Copper Solubility
Effect of DIC
pH
5 mg C/L
10 mg C/L
6.5
7.0
8.0
9.0

Copper Solubility, pH 9

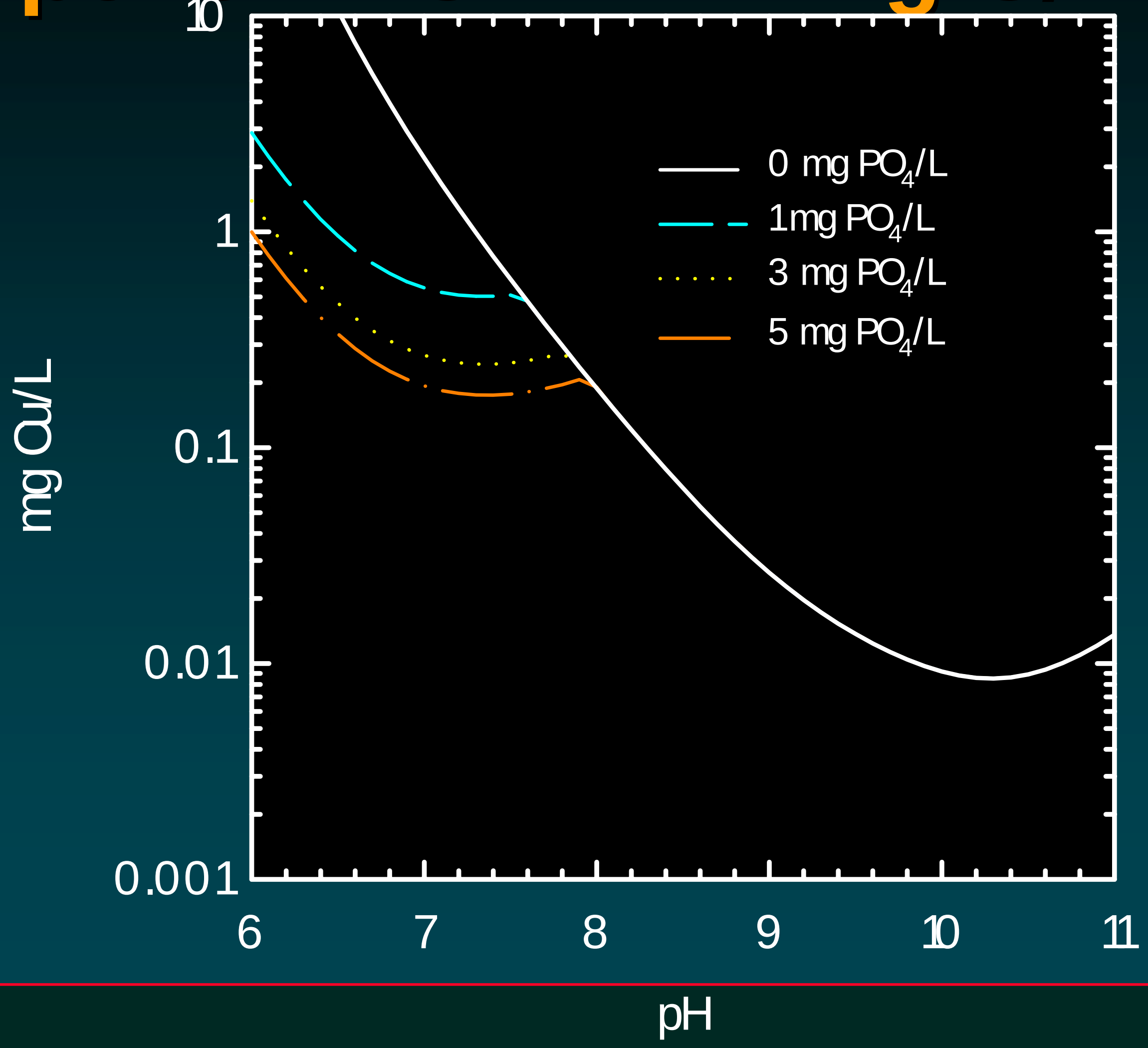


Effect of Orthophosphate

Effect of Orthophosphate on Aged Copper Solubility for DIC=4.8 mg/L

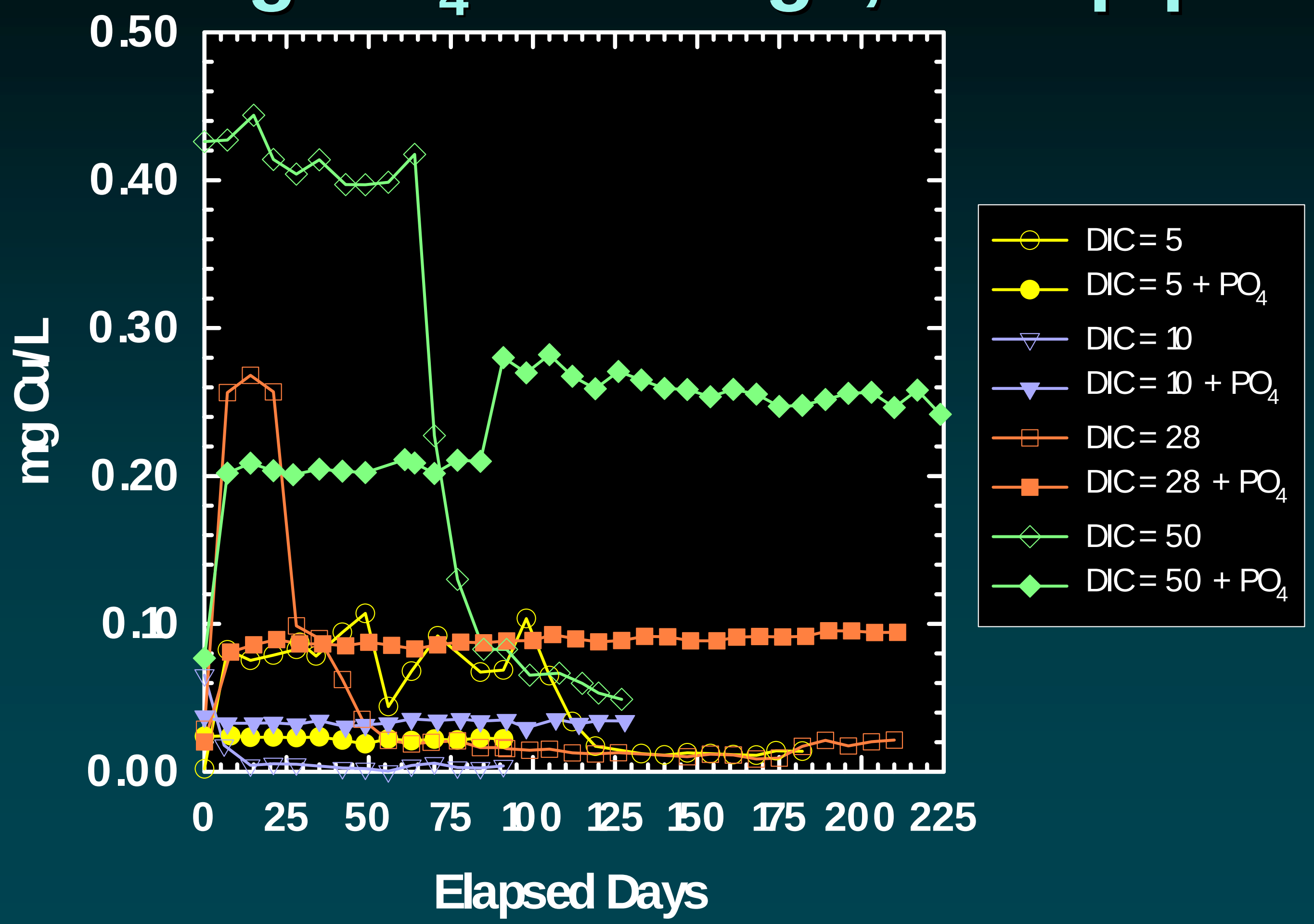


Phosphate Effect on Newer Copper Pipe for DIC = 14.4 mg C/L



Effect of Orthophosphate at pH 9

3.0 mg PO_4/L Dosage, new pipe



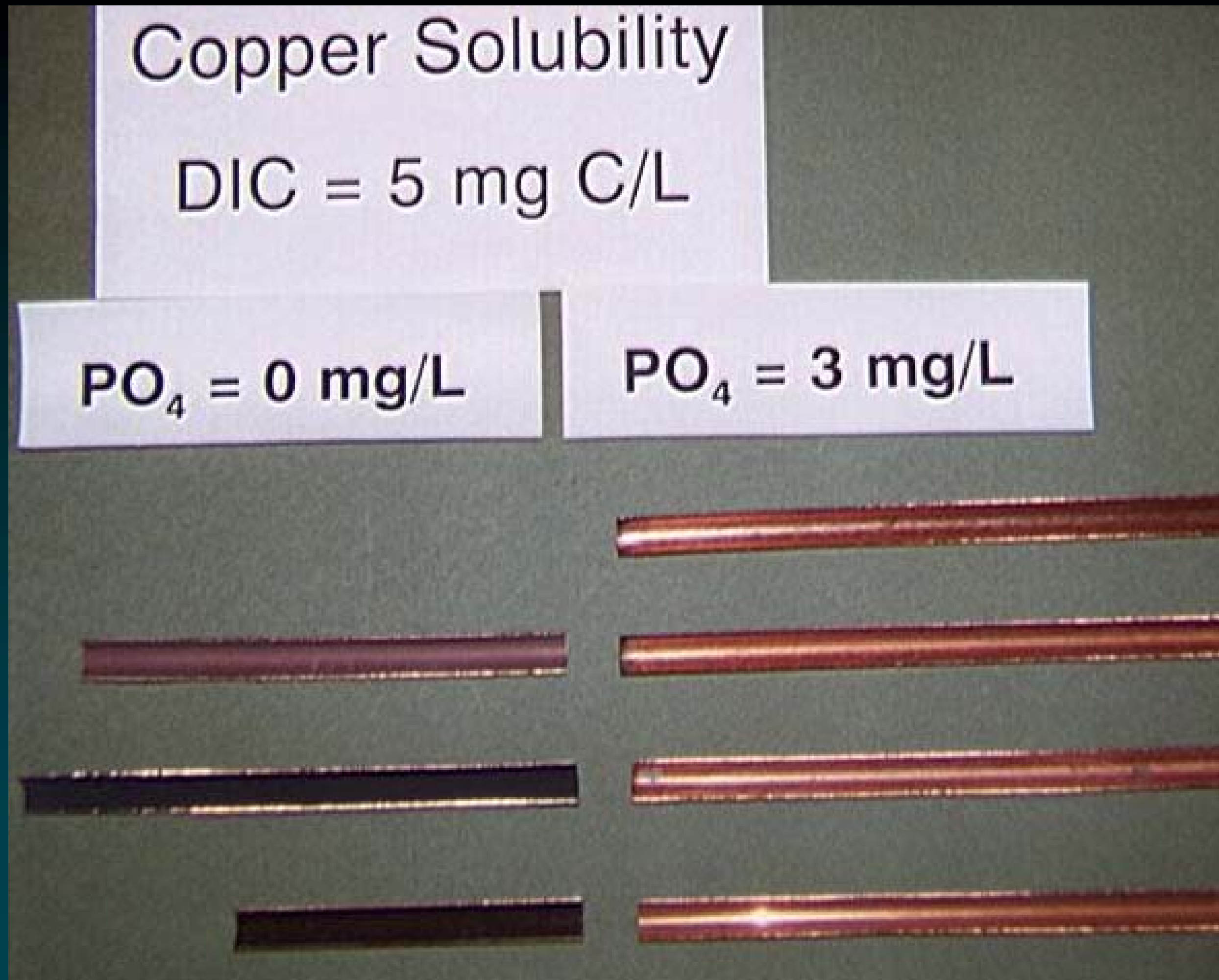
pH

6.5

7.0

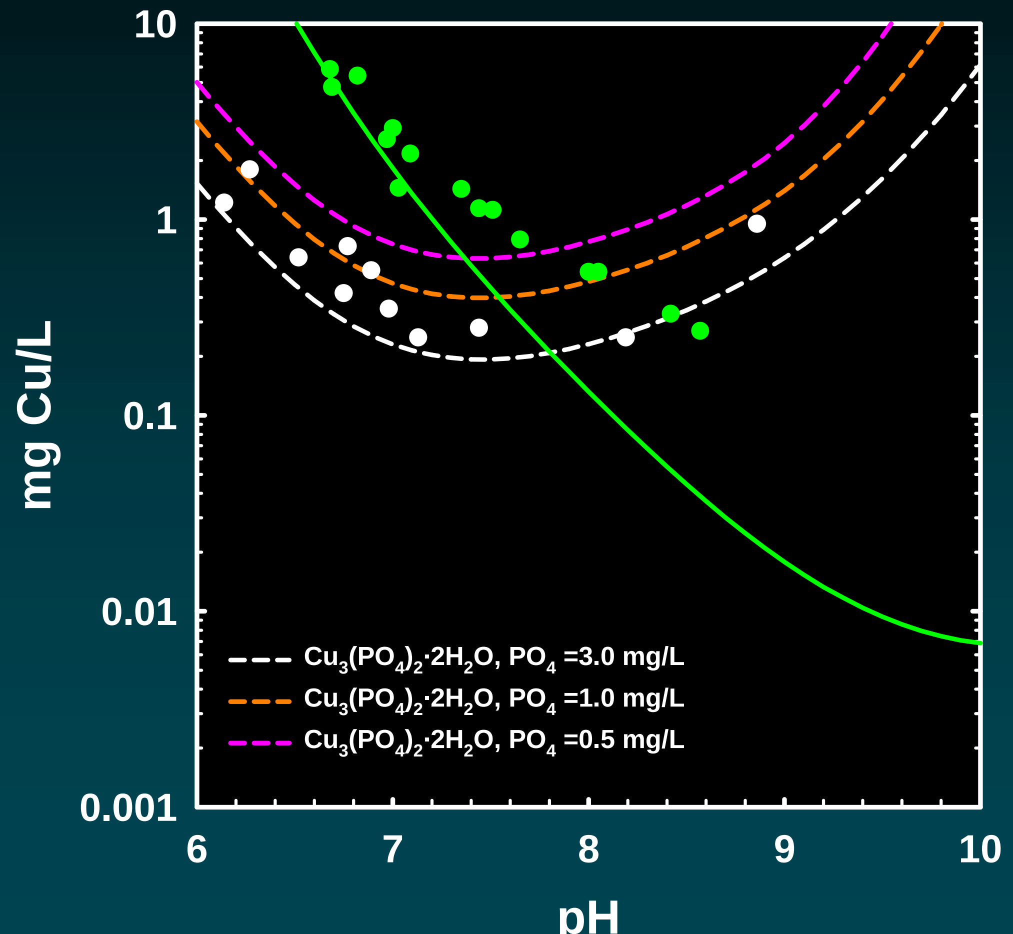
8.0

9.0

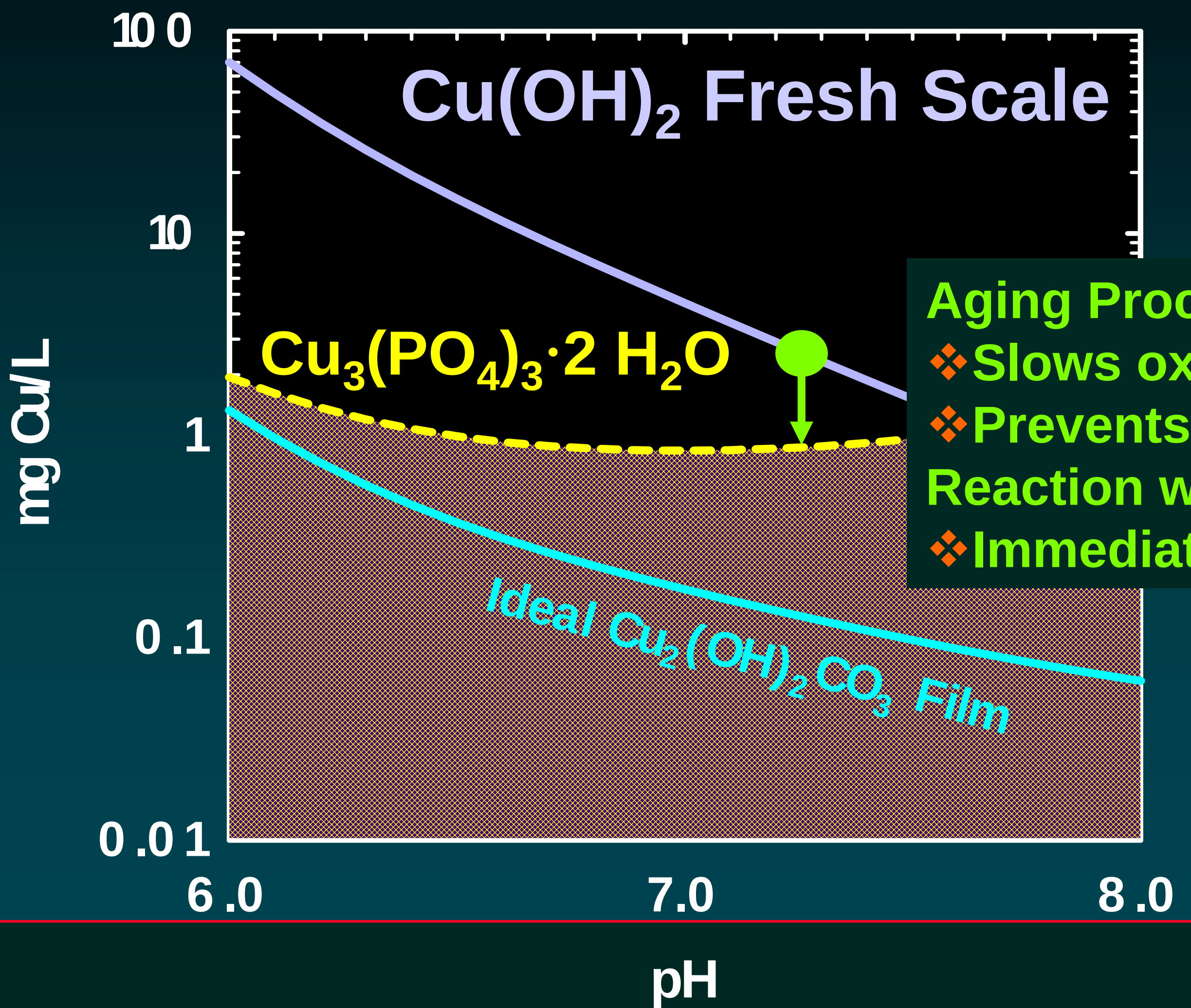


Precipitation Studies

DIC=10 mg C/L, I=0.01, 25^{O}C

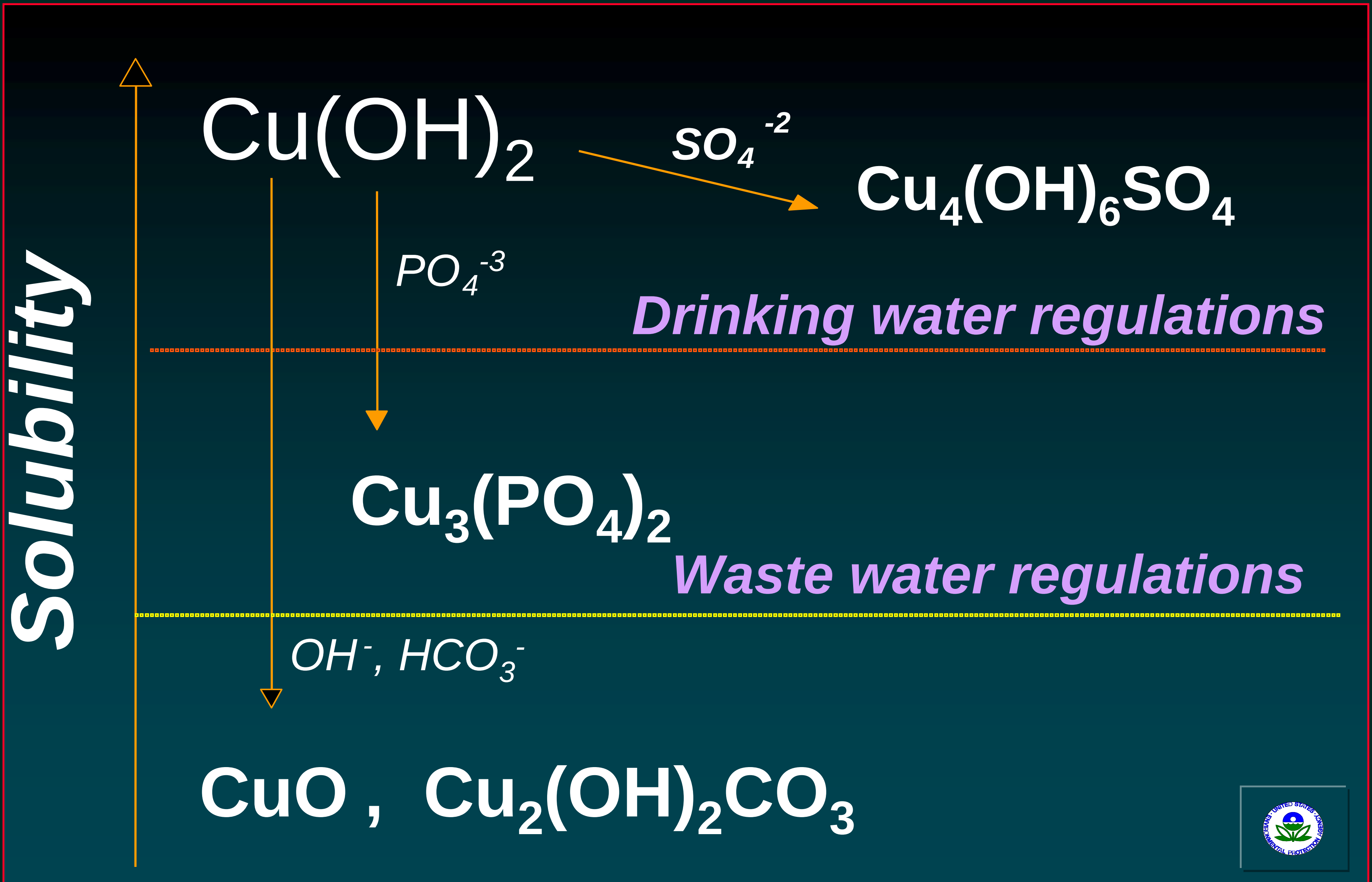


Orthophosphate Effect on Scale Evolution at High DIC



Aging Process is Impeded:

- Slows oxidation
- Prevents or Drastically Slows Reaction with CO_3 or HCO_3^-
- Immediate Benefit


Solubility
$Cu(OH)_2$
SO_4^{-2}
$Cu_4(OH)_6SO_4$
PO_4^{-3}
Drinking water regulations
$Cu_3(PO_4)_2$
Waste water regulations
OH^-, HCO_3^-
CuO , $Cu_2(OH)_2CO_3$

Orthophosphate Effects-Summary

- Tends to sorb to surface or form thin film.
- Inhibits oxidation rate of Cu(I) to Cu(II)
- Inhibits growth of protective CuO at high pH
- Inhibits growth of malachite at low pH
- May reduce copper solubility at low pH, but increase it at high pH

Significance of Metastability

- Copper levels controlled by minerals that are dynamically changing
- Certain anions drastically change nature of passivation film and copper release
- Copper levels normally measured represent disequilibrium: biases could be + or -
- Speciation models need adjustment numerically and in components

Significance of Metastability

- Short-term reductions in copper may conflict with optimum long-term treatment
- Optimal pH/DIC conditions to foster fastest malachite formation largely unknown

Future Research Needs

- What do “short and long term” mean?
- What are the critical levels of each anion?
- What if more than OH^- + 1 anion added?
- Role of pH in anion effects?
- Can we practically speed up aging?

The Regulatory Balancing Act

The Regulatory Balancing Act

- Can changes in coagulation type (e.g. alum to ferric chloride, or PACl) affect lead levels?
  - Mechanism?
    - Scale solubility?
    - Destabilization by charge differences?

The Regulatory Balancing Act

- What is the point of practical tradeoff between pH stability (buffer intensity) and possible increases in plumbosolvency or Pb release through added carbonate complexation?

The Regulatory Balancing Act

- To what extent does orthophosphate or polyphosphate(s) interact with residual aluminum?
  - Reduction of effectiveness of ortho-P for Pb or Cu control?
  - Formation of Al deposit reducing release
  - Adverse effect on hydraulics and aesthetics

The Regulatory Balancing Act

- Corollary questions:
  - Does a solid material form?
  - Does the material have detrimental hydraulics effects?
  - Which species are involved?
  - Can the films be removed without detrimental effects on Pb or Cu?
  - If Al-based, does type of coagulant matter?

The Regulatory Balancing Act

- Are the products of chlorination or “advanced” oxidation of NOM more or less detrimental to lead release than “naturally-occurring” NOM species?
  - Is O_3 without BAF detrimental?
  - Does the effect vary if pH/DIC is used as opposed to phosphate dosing for control.

The Regulatory Balancing Act

Fe/Mn interactions

- Do high redox potentials caused by high DO levels (post O_3) or Fe/Mn oxidation favor rapid passivation by PbO_2?
- What are the relative advantages and disadvantages of oxidation and physical removal vs. sequestration for different waters

The Regulatory Balancing Act

- What are the impacts of different types of phosphates on the passivation and lime leaching from cement pipes and linings?
  - Phosphate chemical species effects
  - Background water chemistry effects?

The Regulatory Balancing Act

- How important is overall Pb/Cu control optimization to levels beyond drinking water requirements to satisfy wastewater discharge and sludge limits?
- Is more wastewater process research needed to optimize P, Zn, Cu, etc. removal?
- What are the impacts of different treatment approaches on hot water systems?

Significance of Metastability

- Short-term reductions in copper may conflict with optimum long-term treatment
- Optimal pH/DIC conditions to foster fastest malachite formation largely unknown

Saturation Index

($Cu(OH)_2$ or CuO)

$$Cu(OH)_2 + 2H^+ \rightleftharpoons Cu^{2+} + 2H_2O$$

$$CuO + 2H^+ \rightleftharpoons Cu^{2+} + H_2O$$

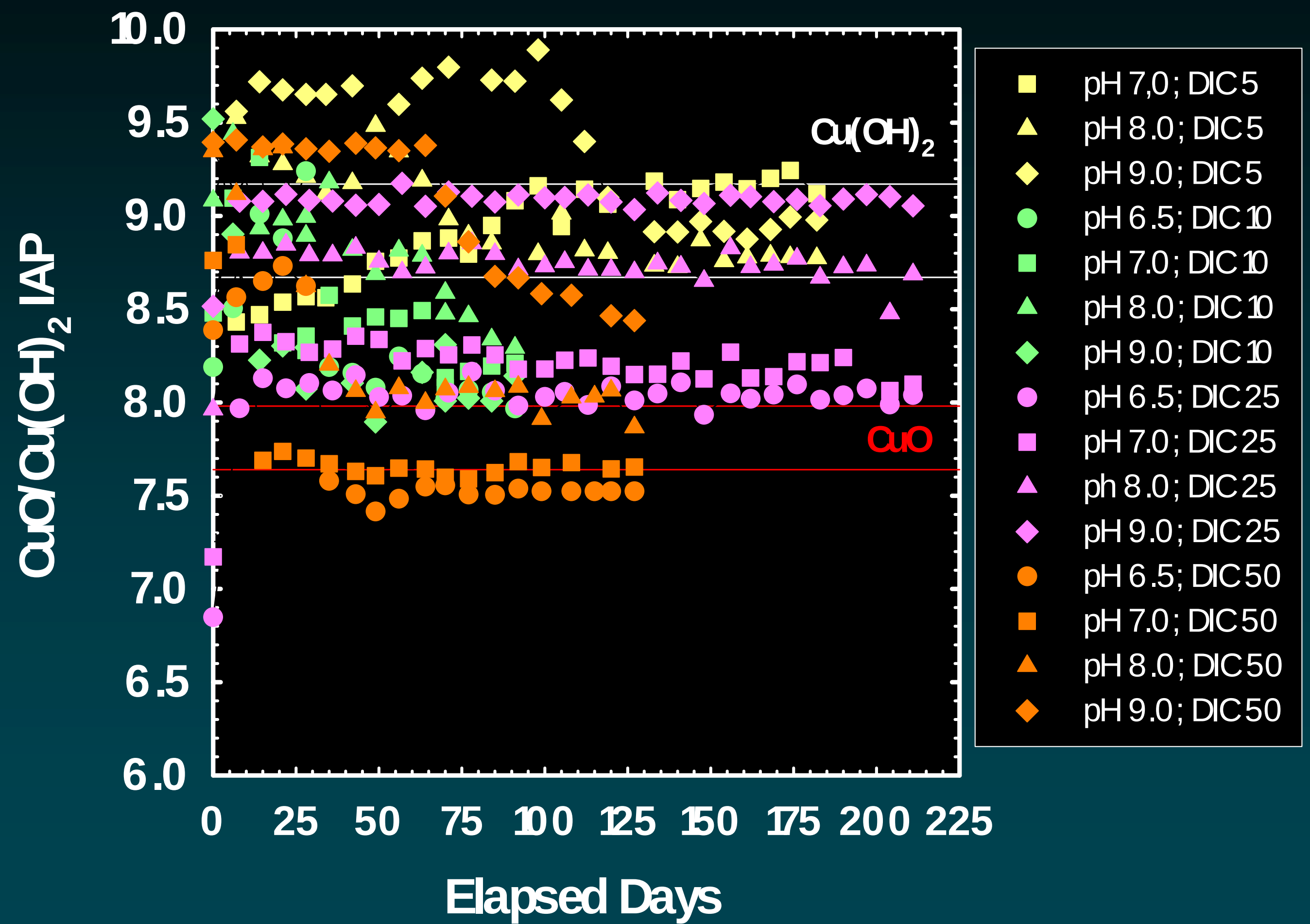
$$SI = \log\left[\frac{\dfrac{\{Cu^{2+}\}}{\{H^+\}^2}}{K_{sp}}\right]$$

Saturation Index
(Malachite)

$$Cu_2(OH)_2CO_3 + 2H^+ \rightleftharpoons 2Cu^{2+} + CO_3^{2-} + 2H_2O$$

$$SI = \log\left(\frac{\dfrac{\{Cu^{2+}\}^2\{CO_3^{2-}\}}{\{H^+\}^2}}{K_{sp}}\right)$$

(Metastable) Ion Activity Products



Lead and Copper Rule: US

- First proposed: 1988
- Covers all public water supplies and non-transient non-community supplies
  - 75,000+ total public water systems
  - 680+ over 50,000 population
  - Administered at State level for 49 of 50
- Substantially revised and promulgated: 1991

Regulatory Approach

- “Treatment Technique” rather than hard MCL for large systems
- Sampling scheme intentionally biased for site selection

Regulatory Approach

- “Action Level” is trigger
  - Optimization of corrosion control (large)
  - Corrosion control studies and treatment to meet 0.015 mg/L for others
  - Public education
  - Possible service line replacement
- Must meet other SDWA regulations at same time

Sulfate Effects-Summary

- May form basic sulfate solid preferentially
- May interfere with normal aging of cupric hydroxide
- Tends to make cuprosolvency less responsive to pH above about pH 7.5 or 8

Speciation Modeling

- WATEQX program
  - Compute Saturation Indices
  - Compute Ion Activity Products
- Refine choice of species
- Refine choice of constants
  - Solubility
  - Formation (aqueous species)

Sulfate Effect at High pH

(Coupon Study) DIC=11-18 mg C/L, SO_4=60-120